

10/038,006

FILE 'HOME' ENTERED AT 18:01:41 ON 27 SEP 2004

=> FILE REG

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'REGISTRY' ENTERED AT 18:01:49 ON 27 SEP 2004

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STRUCTURE FILE UPDATES: 26 SEP 2004 HIGHEST RN 752189-88-1

DICTIONARY FILE UPDATES: 26 SEP 2004 HIGHEST RN 752189-88-1

TSCA INFORMATION NOW CURRENT THROUGH MAY 21, 2004

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<http://www.cas.org/ONLINE/DBSS/registryss.html>

=>

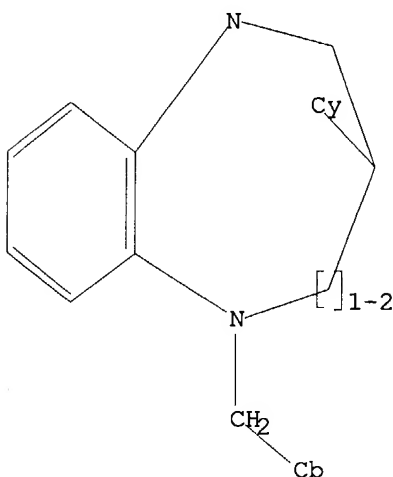
Uploading C:\Program Files\Stnexp\Queries\038006.str

L1 STRUCTURE UPLOADED

=> D L1

L1 HAS NO ANSWERS

L1 STR



Structure attributes must be viewed using STN Express query preparation.

10/038,006

=> S L1 SSS FULL  
FULL SEARCH INITIATED 18:02:10 FILE 'REGISTRY'  
FULL SCREEN SEARCH COMPLETED - 108866 TO ITERATE

100.0% PROCESSED 108866 ITERATIONS  
SEARCH TIME: 00.00.02

5 ANSWERS

L2 5 SEA SSS FUL L1

=> FILE CAPLUS  
COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
155.42	155.63

FULL ESTIMATED COST

FILE 'CAPLUS' ENTERED AT 18:02:21 ON 27 SEP 2004  
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FILE COVERS 1907 - 27 Sep 2004 VOL 141 ISS 14  
FILE LAST UPDATED: 26 Sep 2004 (20040926/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> S L2  
L3 1 L2

=> D L3 IBIB ABS HITSTR

L3 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2004 ACS on STN  
ACCESSION NUMBER: 1999:234566 CAPLUS  
DOCUMENT NUMBER: 131:44796  
TITLE: Solid-Phase Synthesis of 3,4,5-Substituted  
1,5-Benzodiazepin-2-ones  
AUTHOR(S): Lee, Jung; Gauthier, Diane; Rivero, Ralph A.  
CORPORATE SOURCE: The R.W. Johnson Pharmaceutical Research Institute,  
Spring House, PA, 19477, USA  
SOURCE: Journal of Organic Chemistry (1999), 64(9), 3060-3065  
CODEN: JOCEAH; ISSN: 0022-3263  
PUBLISHER: American Chemical Society  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
OTHER SOURCE(S): CASREACT 131:44796

AB The preparation of 3,4,5-substituted 8-carboxamido-1,5-benzodiazepin-2-ones using a solid-phase synthetic method is described. 4-Fluoro-3-

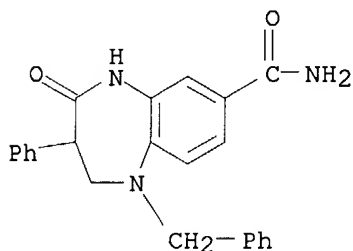
nitrobenzoic acid is tethered to a solid support via the acid group. Aromatic substitution of the aryl fluoride with either an  $\alpha$ - or  $\beta$ -substituted  $\beta$ -amino ester is carried out in the presence of DIEA in DMF. The reduction of the aryl nitro group is accomplished in the presence of  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ . Hydrolysis of the ester is carried out in the presence of a heterogeneous mixture of 1 N NaOH/THF (1:1). The resulting aniline acid is cyclized to form the benzodiazepinone skeleton with DIC and HOBT. Selective alkylation at the N-5 position of the benzodiazepinone is accomplished with alkyl halides in the presence of  $\text{K}_2\text{CO}_3$  in acetone. The desired products are cleaved from solid supports and obtained in 46-98% isolated yields.

IT **224812-11-7P 224812-13-9P 224812-15-1P**  
**224812-17-3P 224812-19-5P**

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (solid-phase synthesis of benzodiazepinones)

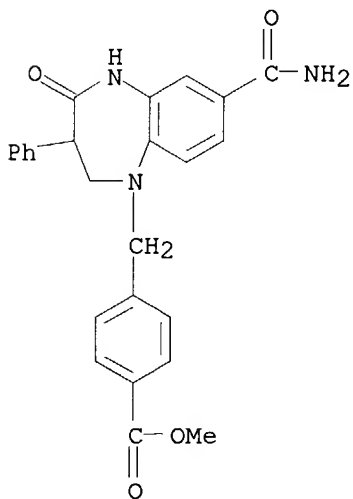
RN 224812-11-7 CAPLUS

CN 1H-1,5-Benzodiazepine-7-carboxamide, 2,3,4,5-tetrahydro-4-oxo-3-phenyl-1-(phenylmethyl)- (9CI) (CA INDEX NAME)



RN 224812-13-9 CAPLUS

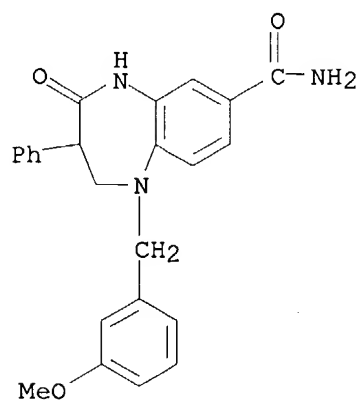
CN Benzoic acid, 4-[[7-(aminocarbonyl)-2,3,4,5-tetrahydro-4-oxo-3-phenyl-1H-1,5-benzodiazepin-1-yl]methyl]-, methyl ester (9CI) (CA INDEX NAME)



RN 224812-15-1 CAPLUS

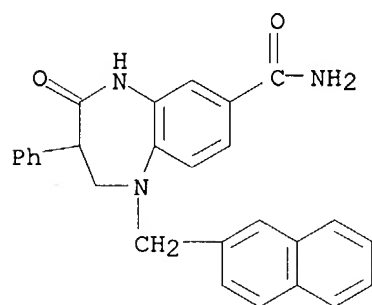
CN 1H-1,5-Benzodiazepine-7-carboxamide, 2,3,4,5-tetrahydro-1-[(3-methoxyphenyl)methyl]-4-oxo-3-phenyl- (9CI) (CA INDEX NAME)

10/038,006



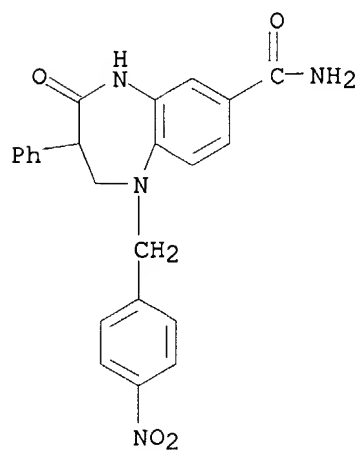
RN 224812-17-3 CAPLUS

CN 1H-1,5-Benzodiazepine-7-carboxamide, 2,3,4,5-tetrahydro-1-(2-naphthalenylmethyl)-4-oxo-3-phenyl- (9CI) (CA INDEX NAME)



RN 224812-19-5 CAPLUS

CN 1H-1,5-Benzodiazepine-7-carboxamide, 2,3,4,5-tetrahydro-1-[(4-nitrophenyl)methyl]-4-oxo-3-phenyl- (9CI) (CA INDEX NAME)



REFERENCE COUNT:

44

THERE ARE 44 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

10/038,006

=> file reg

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

5.20

160.83

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE

TOTAL

ENTRY

SESSION

CA SUBSCRIBER PRICE

-0.70

-0.70

FILE 'REGISTRY' ENTERED AT 18:02:43 ON 27 SEP 2004

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=>

Uploading C:\Program Files\Stnexp\Queries\038006b.str

L4 STRUCTURE UPLOADED

=>

Uploading C:\Program Files\Stnexp\Queries\038006a.str

L5 STRUCTURE UPLOADED

=> s 14

SAMPLE SEARCH INITIATED 18:10:10 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 12909 TO ITERATE

7.7% PROCESSED 1000 ITERATIONS  
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)  
SEARCH TIME: 00.00.01

0 ANSWERS

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 251375 TO 264985

PROJECTED ANSWERS: 0 TO 0

L6 0 SEA SSS SAM L4

=> s 15

SAMPLE SEARCH INITIATED 18:10:16 FILE 'REGISTRY'

10/038,006

SAMPLE SCREEN SEARCH COMPLETED - 14387 TO ITERATE

7.0% PROCESSED 1000 ITERATIONS 0 ANSWERS  
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)  
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*  
BATCH \*\*COMPLETE\*\*  
PROJECTED ITERATIONS: 280558 TO 294922  
PROJECTED ANSWERS: 0 TO 0

L7 0 SEA SSS SAM L5

=> file reg		
COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	7.14	167.97
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	0.00	-0.70

FILE 'REGISTRY' ENTERED AT 18:12:54 ON 27 SEP 2004  
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STRUCTURE FILE UPDATES: 26 SEP 2004 HIGHEST RN 752189-88-1  
DICTIONARY FILE UPDATES: 26 SEP 2004 HIGHEST RN 752189-88-1

TSCA INFORMATION NOW CURRENT THROUGH MAY 21, 2004

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Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more  
information enter HELP PROP at an arrow prompt in the file or refer  
to the file summary sheet on the web at:  
<http://www.cas.org/ONLINE/DBSS/registryss.html>

=>  
Uploading C:\Program Files\Stnexp\Queries\038006d.str

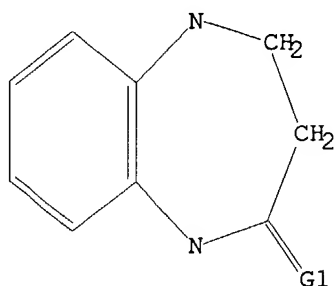
L8 STRUCTURE UPLOADED

=>  
Uploading C:\Program Files\Stnexp\Queries\038006c.str

L9 STRUCTURE UPLOADED

=> d l8  
L8 HAS NO ANSWERS  
L8 STR

10/038,006



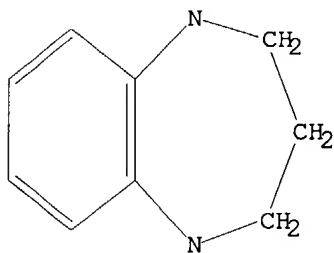
G1 O,S,N

Structure attributes must be viewed using STN Express query preparation.

=> d 19

L9 HAS NO ANSWERS

L9 STR



Structure attributes must be viewed using STN Express query preparation.

=> s 18 sss full

FULL SEARCH INITIATED 18:16:56 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 8820 TO ITERATE

100.0% PROCESSED 8820 ITERATIONS

684 ANSWERS

SEARCH TIME: 00.00.01

L10 684 SEA SSS FUL L8

=> s 19 sss full

FULL SEARCH INITIATED 18:17:05 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 9942 TO ITERATE

100.0% PROCESSED 9942 ITERATIONS

293 ANSWERS

SEARCH TIME: 00.00.01

L11 293 SEA SSS FUL L9

=> file caplus

COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
312.94	480.91

FULL ESTIMATED COST

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE	TOTAL
ENTRY	SESSION

10/038,006

obtain CA references citing the substance. The substance formats must be cited first. The CA File predefined formats are:

ABS -- Abstract  
APPS -- Application and Priority Information  
BIB -- CA Accession Number, plus Bibliographic Data  
CAN -- CA Accession Number  
CBIB -- CA Accession Number, plus Bibliographic Data (compressed)  
IND -- Index Data  
IPC -- International Patent Classification  
PATS -- PI, SO  
STD -- BIB, IPC, and NCL

IABS -- ABS, indented, with text labels  
IBIB -- BIB, indented, with text labels  
ISTD -- STD format, indented

OBIB ----- AN, plus Bibliographic Data (original)  
OIBIB ----- OBIB, indented with text labels

SBIB ----- BIB, no citations  
SIBIB ----- IBIB, no citations

The ALL format gives FIDE BIB ABS IND RE, plus sequence data when it is available.

The MAX format is the same as ALL.

The IALL format is the same as ALL with BIB ABS and IND indented, with text labels.

For additional information, please consult the following help messages:

HELP DFIELDS -- To see a complete list of individual display fields.  
HELP FORMATS -- To see detailed descriptions of the predefined formats.  
ENTER DISPLAY FORMAT (IDE):end

=> d 112 122 ibib abs hitstr

L12 ANSWER 122 OF 122 CAPLUS COPYRIGHT 2004 ACS on STN  
ACCESSION NUMBER: 1958:77247 CAPLUS  
DOCUMENT NUMBER: 52:77247  
ORIGINAL REFERENCE NO.: 52:13730b-i,13731a-i,13732a-c  
TITLE: Cyclic oxo amines. III. Reactions of substituted  
1,2,3, 4-tetrahydro-4-oxoquinolines and of  
1,6-dioxojulolidines  
AUTHOR(S): Ittyerah, P. I.; Mann, Frederick G.  
CORPORATE SOURCE: Univ. Chem. Lab., Cambridge, UK  
SOURCE: Journal of the Chemical Society, Abstracts (1958)  
467-80  
CODEN: JCSAAZ; ISSN: 0590-9791  
DOCUMENT TYPE: Journal  
LANGUAGE: Unavailable  
OTHER SOURCE(S): CASREACT 52:77247  
AB cf. C.A. 52, 5411c. Earlier studies of the reactions of the above 2 types of keto amines were extended. The structures of the derivs. formed by the action of p-ONC6H4NMe2 (I), by bromination, and by dehydrogenation were elucidated. The action of N2H4 and of HNO3 and the application of the Mannich and the Schmidt reaction were also investigated. The properties of 1,6-dioxoisojuloline (II) were of particular interest.  
1,2,3,4-Tetrahydro-4-oxo-1-methylquinoline (III) (0.3 g.) and 0.3 g.



p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO (IV) in 15 cc. alc. containing 0.1 cc. piperidine refluxed 4 hrs. and cooled gave 0.2 g. 3-p-dimethylaminobenzylidene derivative (V), m. 145° (alc.), of III. The use of NaOH instead of piperidine gave only a sticky product in low yield. 1,2,3,4-Tetrahydro-4-oxo-1-phenylquinoline (VI) (0.3 g.) and 0.3 g. IV in alc. containing 0.2 cc. 10% aqueous

NaOH refluxed 1 hr. and set aside overnight gave 0.4 g. 3-p-dimethylaminobenzylidene derivative (VII), m. 148-50° (Me<sub>2</sub>CO). The use of piperidine instead of NaOH gave only unchanged VI. I (0.3 g.) in 5 cc. alc. added dropwise to 0.3 g. III in 5 cc. alc. diluted with 2 cc. 10% NaOH at 60° gave 3-(p-dimethylaminoanilino)-1,4-dihydro-1-methyl-4-oxoquinoline, needles, m. 215° (alc.). A similar experiment with VI gave 75% 1-Ph analog, m. 175°. VI (0.7 g.), 0.5 g. 2-quinolinecarboxaldehyde, and 0.1 g. KOH in 15 cc. alc. refluxed 2 hrs. gave 1 g. 1-phenyl-3-(2-quinolylmethylene)-4-oxo derivative, m. 205°. III (1.6 g.) in 30 cc. CCl<sub>4</sub> shaken 2 hrs. with 1.7 g. N-bromosuccinimide (VIII) gave 1.9 g. 6-bromo-1,2,3,4-tetrahydro-1-methyl-4-oxoquinoline (IX), m. 85° (alc.). IX refluxed 1 hr. in aqueous alc.-KOH gave unchanged material. IX treated with IV in alc. containing piperidine gave the orange 3-(p-dimethylaminobenzylidene) derivative, m. 165°. A similar experiment with I in alc. containing 10% NaOH gave the yellow 3-(p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH) derivative, m. 281°. VI similarly treated gave the 6-Br derivative (X), m. 95-100° (alc.), unaffected by refluxing aqueous KOH. X gave the yellow 3-(p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH) derivative, m. 210° (alc.). With 3.4 g. VIII and 5 mg. Bz<sub>2</sub>O<sub>2</sub> shaken 4 hrs. and left overnight was obtained 2.8 g. of the 6,8-dibromo-1-methyl-4-oxo derivative (XI), m. 126°. XI gave the 3-(p-dimethylaminobenzylidene) product, plates, m. 190° (C<sub>6</sub>H<sub>6</sub> or MeOH), and a yellow 3-(p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH) derivative, m. 225°. III (1 g.), 0.1 g. 10% Pd-C, and 10 cc. (CH<sub>2</sub>OH)<sub>2</sub> refluxed 0.5 hr. and the product treated with picric acid gave the picrate (XII) of 1,4-dihydro-1-methyl-4-oxyquinoline, m. 226°. Repeating the above experiment but using X gave XII. Similarly, VI gave the picrate of the 1-Ph derivative, m. 136° (alc.). III (0.8 g.) 0.6 g. Me<sub>2</sub>NH.HCl, 0.2 g. paraformaldehyde, and 15 cc. Me<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OH refluxed 15 min. and the clear solution treated with 0.3 g. more aldehyde and refluxed a further 0.5 hr. gave 0.8 g. 1,4-dihydro-1,3-dimethyl-4-oxoquinoline, m. 320° (decomposition), sparingly soluble in hot alc., Me<sub>2</sub>CO, and C<sub>6</sub>H<sub>6</sub>. Repetition of this experiment

but

using 1.1 g. VI gave 1 g. 1,4-dihydro-3-methyl-4-oxo-1-phenylquinoline (XIII), darkened at 295° and slowly decomposed at 320-40°, but immersed at 310° it m. 325°. Thus the initial product in this reaction is the tertiary amine-HCl, which breaks off the dialkylamine-HCl to form the 3-methylene derivative, which then isomerizes to the stable XIII. III (0.8 g.) and 0.12 g. pure N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O in 10 cc. alc. containing 0.1 cc. AcOH refluxed 1 hr. gave 0.75 g. N,N'-bis(1,2,3,4-tetrahydro-1-methyl-4-quinolyldiene)azine (XIV), plates, m. 198° (C<sub>6</sub>H<sub>6</sub>). VI in the above experiment gave 73% of the 1-Ph analog, m. 208° (dioxane). XIV in alc. added to a large excess of alc. picric acid deposited the monopicrate, red needles, m. 165° (decomposition). XIV in alc. chilled to 0° and treated with dry HCl gave the red HCl salt. A portion of the red solution treated, before separation of the red crystals, dropwise with cold concentrated HCl gave N<sub>2</sub>H<sub>4</sub>.2HCl, m. 198-200°. Alternatively, a fine suspension of XIV in Et<sub>2</sub>O similarly treated with HCl gave the HCl salt, m. 85-7°; analysis indicated that this was a di-HCl salt. HCl passed 0.5 hr. through molten XIV, initially at 200° and then at 190-200°, gave the di-HCl salt of s-bis(1,2-dihydro-1-methyl-4-quinolyl)hydrazine, m. 295° (decomposition); dipicrate, m. 243° (decomposition) (alc.). Concentrated

H<sub>2</sub>SO<sub>4</sub> (8

cc.) added dropwise to 1.6 g. III in 10 cc. CHCl<sub>3</sub>, the solution stirred a

further 15 min., diluted with 45 cc. cold H<sub>2</sub>O, neutralized, and extracted with Et<sub>2</sub>O gave 1 g.  $\beta$ -[N-(*o*-aminophenyl)-N-methylamino]propionic lactam, needles, m. 170° (C<sub>6</sub>H<sub>6</sub>). VI similarly treated gave 91%  $\beta$ -[N-(*o*-aminophenyl)anilino]propionic lactam, m. 221° (alc. then C<sub>6</sub>H<sub>6</sub>). III (1 g.) in 10 cc. AcOH treated below 15° with a mixture of 1 cc. concentrated HNO<sub>3</sub> and 10 cc. AcOH, set aside 20 min., and poured into H<sub>2</sub>O gave 1.2 g. 6-nitro derivative, needles, m. 169° (alc.); phenylhydrazone, red plates, m. 198° (decomposition) (alc.); 3-(*p*-dimethylaminobenzylidene) derivative, red plates, m. 210° (alc.). *p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> on cyanoethylation gave a low yield of *p*-ClC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub>, which in turn on cyclization gave a small amount of 8-chloro-1,6-dioxojulolidine (XIVa). This difficulty also applies to the Br analog, but *p*-BrC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub> (XV) and 8-bromo-1,6-dioxojulolidine (XVa) can be readily prepared by direct bromination with IX. *p*-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (17 g.), 12 g. CH<sub>2</sub>:CHCN, 12 g. AcOH, and 1.7 g. CuCl refluxed 12 hrs. and poured into 100 cc. NH<sub>3</sub> gave *p*-BrC<sub>6</sub>H<sub>4</sub>NHCH<sub>2</sub>CH<sub>2</sub>CN, b<sub>5</sub> 160°, m. 96-8°; the residue in the flask decomposed at higher temps. This experiment when repeated by refluxing 20 hrs. gave 2 g. above compound and 4 g. XV, m. 94-5° (alc.). PhN(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub> treated 4 hrs. in CCl<sub>4</sub> with 1 mole IX and 0.05 mole Bz<sub>2</sub>O<sub>2</sub> gave 82% XV. XV heated with AlCl<sub>3</sub> in PhCl gave what was apparently 1-(2-cyanoethyl)-1,2,3,4-tetrahydro-4-oxoquinoline, m. 79-81°; phenylhydrazone, m. 250°; 2,4-dinitrophenylhydrazone, m. above 360°. Thus under the conditions used for this monocyclization the nuclear Br was removed. II, 0.6 g. 2-quinolinecarboxaldehyde, 15 cc. alc., and 0.1 g. KOH refluxed 1 hr. gave 0.3 g. 1,6-dioxo-2,5-bis(2-quinolylmethylene)julolidine, m. 185° (C<sub>6</sub>H<sub>6</sub>). The 7,9-di-Me derivative (XVI) of II similarly treated gave the 7,9-di-Me homolog, m. 225° (C<sub>6</sub>H<sub>6</sub>). XVI treated with 2.2 moles IV in refluxing alkali and alc. gave 93% 2,5-bis(*p*-dimethylaminobenzylidene)-7,9-dimethyl-1,6-dioxojulolidine, needles, m. 245° (alc.). XVI similarly treated with 2.1 g. I gave 83% 2-(*p*-dimethylaminoanilino)-5-(*p*-dimethylaminophenylimino)-7,9-dimethyl-1,6-dioxojulolidine (XVII), purple crystals, m. 268° (decomposition) (Me<sub>2</sub>CO). XVII (0.5 g.) refluxed 0.5 hr. with 20 cc. concentrated HCl gave 1.25 g. 7,9-dimethyl-1,2,5,6-tetraoxojulolidine (XVIII), bronze-colored crystals, slowly decomposed at 330°. XVIII resembles the parent member in that it is insol. in all the usual solvents, but soluble in aqueous KOH to give a purple solution

It did

not condense with *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. IX (2 g.) and 0.05 g. Bz<sub>2</sub>O<sub>2</sub> shaken 3 hrs. with 1 g. II in CCl<sub>4</sub> gave 1.2 g. XVa, plates, m. 208°,  $\lambda$  421.5-25.5, 301-2.5, 227, 338.5-40, and 276.5 m $\mu$ ,  $\epsilon$  5130, 4490, 30,100, 252, and 1650. When the mixture was refluxed only a brown amorphous intractable material was obtained. XVa gave a bis(phenylhydrazone), m. 270°. XVa (0.28 g.) and 0.22 g. BzH in 15 cc. alc. and 0.1 cc. piperidine refluxed gave 0.2 g. 2,5-dibenzylidene-8-bromo-1,6-dioxojulolidine, m. 200° (alc.). II treated with 1 mole N-chlorosuccinimide under the above conditions at room temperature gave no reaction, but warming the mixture under reflux 1 hr. gave 68% XIVa, m. 201°. II (1 g.), 0.1 g. 10% Pd-C, and 25 cc. *p*-cymene refluxed 1.5 hrs., a slow stream of CO<sub>2</sub> blown through the solution, and the hot mixture filtered and cooled gave 0.6 g. 1,6-dioxoisojuloline (XIX), m. 202° (lower yields were obtained in expts. on a larger scale); HBr salt, m. 270° (decomposition); picrate, m. 202°; diperchlorate, m. 240° (decomposition). A cold aqueous suspension of this salt with NH<sub>4</sub>OH gave XIX. An alc. solution of the salt treated overnight at 0° with excess HClO<sub>4</sub> gave the normal perchlorate, m. 125°, and these crystals dissolved in hot alc. gave the diperchlorate on cooling; metho-*p*-toluenesulfonate, m. 180° (decomposition); phenylhydrazone-0.5H<sub>2</sub>O, plates, m. 220°. 2-(*p*-Dimethylaminobenzylidene)-1,6-dioxoisojulolidine prepared in refluxing alc. with piperidine formed red

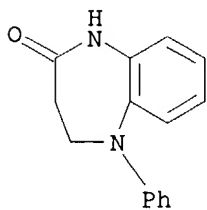
crystals, m. 230° (dioxane). Although the conditions of the above reduction were varied over wide limits no further dehydrogenation could be effected. XIX (0.33 g.), 0.22 g. CH<sub>2</sub>(CN)<sub>2</sub>, 0.1 g. NH<sub>4</sub>OAc, 10 cc. C<sub>6</sub>H<sub>6</sub>, and 1 cc. AcOH refluxed 45 min. gave 1-(dicyanomethylene)-6-oxoisojulolidine, needles, m. 245° (decomposition). Attempted application of the Mannich reaction to II under the above conditions gave solely an intractable powder of indefinite m.p. II (2 moles), 1 mole N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O, and a few drops of AcOH on heating gave a complex orange polymeric mixture, m. 280-320°. II gave a deep yellow mixture XVI (1 g.), 1 g. 100% N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O, 0.5 g. KOH, and (CH<sub>2</sub>OH)<sub>2</sub> refluxed 2 hrs., heated 4 hrs. at 195-200°, the mixture diluted with H<sub>2</sub>O, cooled, the solids collected, extracted with alc., and the exts. evaporated gave with picric acid

a  
picrate, almost certainly julolidine picrate. XVI similarly treated gave the 7,9-dimethyljulolidine picrate, m. 160° (alc.). II in CHCl<sub>3</sub> with H<sub>2</sub>SO<sub>4</sub> and NaN<sub>3</sub> gave 81% dilactam of 2,6-diamino-N,N-bis(2-carboxyethyl)aniline, plates, m. 356° (decomposition) (AcOH). 7-Methyl-1,6-dioxojulolidine (2.1 g.), 3.1 g. isatin, and 3.6 g. KOH in 25 cc. MeOH and 5 cc. H<sub>2</sub>O refluxed 20 hrs. gave 3 g. 7-methyl-6-oxoquinolino(2',3'-1,2)juloline-4'-carboxylic acid (XX), m. 215° (decomposition). XX heated in a tube at 210-20°/0.1 mm. underwent decarboxylation and gave 7-methyl-6-oxoquinolino(2',3'-1,2)juloline, plates, m. 185°, unchanged by further crystallization or sublimation. II (1 g.) in 10 cc. AcOH treated with 1 cc. concentrated HNO<sub>3</sub> below 20° and set aside 20 min. gave 1.2 g. 8-nitro-1,6-dioxojulolidine, m. 250°; bis(phenylhydrazone), m. 270° (decomposition).

IT **32900-17-7**, 2H-1,5-Benzodiazepin-2-one, 1,3,4,5-tetrahydro-5-phenyl- **33035-62-0**, 2H-1,5-Benzodiazepin-2-one, 1,3,4,5-tetrahydro-5-methyl- (preparation of)

RN 32900-17-7 CAPLUS

CN 2H-1,5-Benzodiazepin-2-one, 1,3,4,5-tetrahydro-5-phenyl- (6CI, 8CI, 9CI)  
(CA INDEX NAME)



RN 33035-62-0 CAPLUS

CN 2H-1,5-Benzodiazepin-2-one, 1,3,4,5-tetrahydro-5-methyl- (6CI, 8CI, 9CI)  
(CA INDEX NAME)

